EXHIBIT B

Optimized Materials Properties for Organosilicate Glasses Produced by Plasma-Enhanced Chemical Vapor Deposition

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Abstract

In this paper we examine the relationship between precursor structure and material properties for films produced from several leading organosilicon precursors on a common processing platform. Results from our study indicate that for the precursors tested the nature of the precursor has little effect upon film composition but significant impact on film structure and properties.

Introduction

There are a variety of materials being considered for the next generation interlayer dielectric (ILD) materials. The leading candidates for the 90nm generation are organosilicate glasses produced by Plasma-Enhanced Chemical Vapor Deposition (PECVD). Providing materials with extendibility beyond a single generation solution requires the optimization of both electrical and mechanical properties. These are competing goals since concomitant with reducing the dielectric constant (k) is, in general, a decrease in the mechanical strength of a material.

The goal of this work is to build a better understanding of the structure of low k dielectric films deposited from a PECVD process. In attempts to elucidate structure-property relationships for OSG precursors we assessed a variety of chemicals including those used in various commercial product offerings.

Experimental

All experiments were performed on an Applied Materials Precision 5000 fitted with a 200mm DxZ chamber. Every attempt was made to optimize process regimes for each precursor to provide the best mechanical properties at a given dielectric constant (k). Films were analyzed for refractive index and thickness with a SCI FilmTek 2000 reflectometer calibrated daily. Electrical tests were performed on low resistivity wafers (< .02 ohm-cm) using a mercury probe calibrated with thermal oxide standards of various thicknesses. Errors in film thickness and capacitance contributed to an error of ±5% in k; typical measurement standard deviation was within ±3%. Mechanical properties were evaluated by nanoindentation using a MTS model SA-2 on films greater than 750 nm thick as per manufacturers protocol [1] (multi-sample average, modulus / hardness quoted at 50 / 100nm depth, respectively; measurement error ± 10%, standard deviation typically less than ±5%). Atomic composition by X-ray photoelectron spectroscopy (XPS) was collected on a Physical Electronics 5000LS ESCA spectrometer after Ar beam sputtering to remove the topmost 20Å from the surface of the film. Bonding structure and functional group analyses were performed by transmission FT-IR spectra on high resistivity wafers (> 20 ohm-cm) using a Thermo Nicolet 750 at 4 cm^{-1} resolution, nitrogen purged cell and background corrected with Si. Selected samples were analyzed using Carbon-13 and Silicon-29 Nuclear Magnetic Resonance (NMR). Density

measurements by X-ray reflectivity were preformed by an outside laboratory. All samples were analyzed as-deposited unless noted otherwise.

OSG Comparison

The various organosilicon precursors tested are shown in Table 1. Their compositions and structures varied in the type and amount of substituents to Si. All of these precursors were able to provide films with k as low as 2.7, though some required widely different process conditions. The trends for most precursors follows a power per molecule relationship [2, 3] whereby decreased precursor flow rate, decreased pressure, and

Molecule	SI–CH₃:SI	SI–O:SI	Si–H:SI	Structure
DEMS	1:1	2:1	1:1	
TMCTS	1:1	1:1	1:1	
DMDMOS	2:1	2:1	N/A	
3MS	3:1	N/A	1:1	

Table 1. Organosilocon precursors tested in this study

increased power or spacing all function to reduce carbon content of the deposited material and generally provide higher k and mechanical properties. In general depositions were performed at the highest temperature possible (e.g. 425 °C). This is because increases in temperature generally provide mild increases in k but significant improvements in mechanical strength. Also, most data analysis shown were performed on films from depositions which did not include added oxidants; the exception was trimethylsilane which requires an added oxidant to produce an organosilicate material.

The composition of the optimum films produced from the OSG precursors with various k values are listed in Table 2. All materials with k in the range of 3.0-3.3 have a C:Si ratio of ~1:2, indicating that only half of the Si atoms have C substituents. Regardless of carbon content of the precursor, at equivalent k optimized materials from this study have essentially equivalent composition.

Precursor (k)	%C	%O	%Si
DEMS (3.2)	18	47	35
DEMS (3.0)	18	48	34
DEMS (2.7)	21	46	33
TMCTS (2.9)	18	47	35
TMCTS (2.7)	21	44	35
DMDMOS (3.3)	18	47	35
DMDMOS (3.1)	21	44	35
DMDMOS (2.8)	23	42	35
3MS (2.9)	23	42	35

Table 2. XPS compositions from various precursors (+/- 1 atomic %)

Although at a given k there is essentially no change in composition for each sample regardless of precursor, there are rather large changes in mechanical strength and structure analysis by FT-IR for films tested in this study. Films produced from DMDMOS, for example, provide greater than threefold increase in mechanical properties as k increases from 2.8 to 3.3. The relative oxide content was determined from integration of the entire Si-O absorption region (approximately 1250 to 1000 cm⁻¹) of FT-IR spectra for each film and normalized to thickness. Integrating the region from approximately 1300 to 1250 cm⁻¹, thereby incorporating single and multiple methyl substitutions on Si, and normalizing to thickness and to Si-O absorption was used to provide a measure of methyl content relative to Si-O content. The relative methylene bridge content per Si-O unit was determined similarly by

integrating the region from approximately 1390 to 1330 cm^{-1}. It is assumed that the extinction coefficients for these species do not vary significantly between materials.

While there are significant differences in IR spectra seen between the various precursors, there are relatively few structural changes in the spectra at various k for a given precursor. A comparison of the measurements for films produced from DEMS, DMDMOS, TMCTS, and 3MS at k=2.9-3.1 range are shown in Figure 1. Our work indicates that DEMS provides the highest mechanical properties of the OSG precursor tested. Differences in the materials are exemplified in the expanded view of the Si-O region of the respective FT-IR spectra shown in Figure 2. There are variations in the absorption maximum from 1043 cm^{-1} for DEMS to 1034 cm^{-1} for DMDMOS, both substantially shifted from that observed for TEOS-oxide at 1076 cm^{-1}. Analysis of the relative integrated areas for Si-O indicates that the DEMS film provides a significantly higher total absorbance than the other precursors, suggestive of a high network density for DEMS films. Relative to TEOS-oxide the DEMS film provides ~ 70% of the Si-O absorption. X-ray reflectivity measurements indicate that the density of DEMS films is 10% higher than the density of a 3MS film at a k of approximately 3 (1.49 vs. 1.35 g/cc, respectively), and having a density of ~ 1.6 g/cc at k=3.2. Also, the refractive index (632 nm) for DEMS

Figure 1. Structure-property comparison for OSG precursors

Figure 2. Expanded view of Si-O region at k ~3.0 (not normalized)

film are approximately 1.47, significantly higher than that for 3MS (~1.42) and TMCTS (1.40). The data indicates a direct relationship between Si-O absorption intensity, film density, and mechanical properties. From this data it appears that the nature of the precursor has a large impact upon the ability to produce an optimized organosilicate structure.
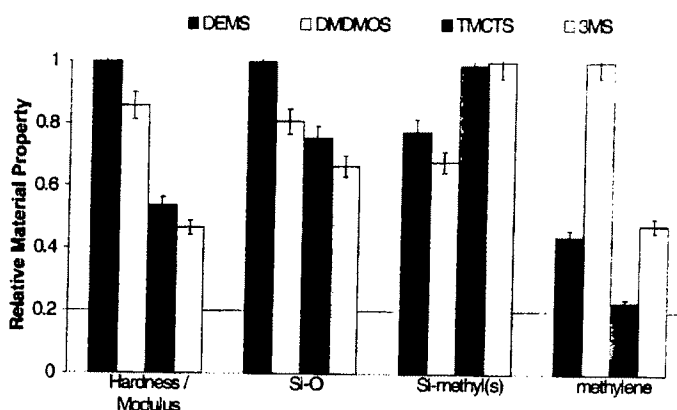
Analysis of the methyl region of the FT-IR for the films produced at k=2.9-3.1 indicates that 3MS in particular imparts a significant amount of multi-methyl substituted Si to the network as noted by a strongly non-symmetrical absorption due to a low energy shoulder at ~ 1260 cm^{-1}. The ^{29}Si NMR spectra shown in Figure 3 further verifies that these 3MS materials include a substantial population of trimethlysilyl species. The relatively minor presence of dimethylsilyl species in DEMS is also somewhat evident in the FT-IR

Figure 3. ^{29}Si NMR comparison of DEMS and 3MS films at k~3.0

spectrum, indicating that molecular rearrangements are substantial during the deposition process. The data shown in Figure 1 also indicates that 3MS and TMCTS produce films containing higher methyl content. Our molecular modeling work indicates there is relatively little benefit to k by increasing methyl group concentration beyond a Si:CH$_3$ ratio of 2:1. However, there is a significant negative impact on mechanical strength that increasing the methyl concentration has due to replacement of network bonds with terminal groups [4]. Our data supports this hypothesis as films from 3MS and TMCTS at equivalent k contain higher methyl content and lower mechanical strength. This indicates that an optimum methyl content exists for OSG materials that balances the effects of organic groups on the dielectric and mechanical properties of the film.

Molecular modeling also suggests that methylene groups, e.g. Si-CH$_2$-Si, should improve the mechanical strength of OSG films by increasing networking relative to terminal methyl groups yet still be somewhat effective in providing a low k material [5]. The relative integrated methylene regions shown in Figure 1 indicate that the DMDMOS film contains almost three times the amount of methylene content at equivalent k relative to the other precursors tested. This is exemplified in Figure 4 by the relative absorptions at 1360 cm^{-1} (Si-methylene) and 1410 cm^{-1} (Si-methyl). Since the extinction coefficient of the methylene group is considered to be small [5], there likely exists a substantial amount of bridging carbon in films produced

Figure 4. Expanded view of the Si-CH$_2$-Si region (not normalized)

from DMDMOS in this study. The high methylene content is likely somewhat responsible for the superior mechanical strength of DMDMOS films relative to 3MS and
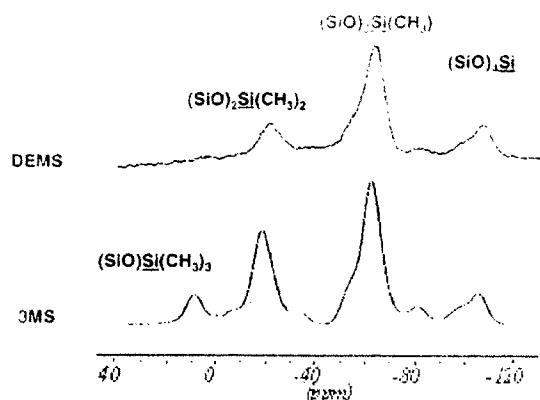
TMCTS films in this study. It is proposed that the mechanical strength of films with excess methyl content could be enhanced by converting a portion of the terminal methyls to bridging methylene with little negative impact on k. By comparison to DEMS, the contribution of methylene found in DMDMOS films produced in this study is not sufficient to overcome the impact that the high Si-O content has on mechanical strength.

Analysis of the region between 2100 and 2300 cm^{-1} in Figure 5 shows that all the films in this study except TEOS-oxide have considerable Si-H content. Despite the lack of Si-H in the DMDMOS molecule, analysis of the Si-H regions indicates that films from DMDMOS produced in this study have the highest hydride content: 25% greater than TMCTS, 40% greater than DEMS, and 50% greater than 3MS (assuming equivalent extinction coefficient for the 2175 and 2235 cm^{-1} absorptions). As seen in Figure 5 films from DMDMOS are unique in that they show a larger absorption at ~ 2175 cm^{-1} due to hydride species with adjacent organic (methyl, methylene, etc...) groups. This indicates that H replaces significant portions of the methyl groups in DMDMOS during the deposition. Regardless of the origin, the increased presence of non-network forming groups such as hydride will negatively impact mechanical strength.
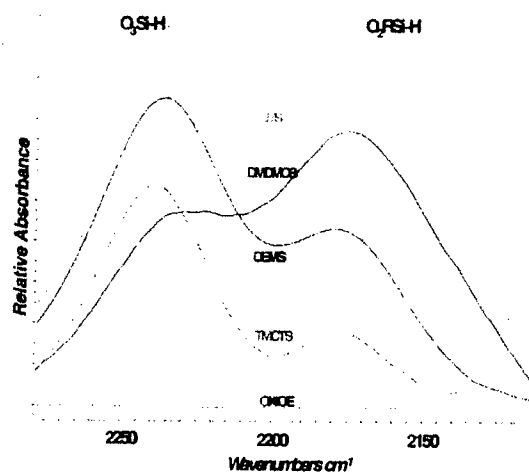

Figure 5. Expanded view of the Si-H region (not normalized)

DEMS Comparison

The relationship between film structure and properties was studied in detail for DEMS films at k between 2.7 and 3.2. The results are shown in Figure 6. The significant differences in IR spectra seen between the various precursors and relatively few change in the spectra for a given precursor over a k range suggests a strong correlation between precursor and film structure. For DEMS, as k increases from 2.7 to 3.2 a 15% increase in Si-O content is seen by FT-IR analysis. The shape
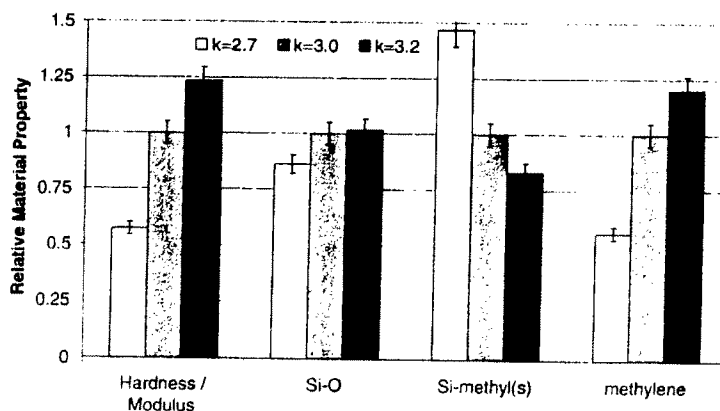

Figure 6. Structure- property comparison for DEMS

of the Si-O absorption changes slightly with k due to the impact that organic group content has on the Si-O absorption, as seen by changes in the relative absorptions at approximately 1040 and 1130 cm^{-1}. The reduction in carbon content from 21 to 18 at % as k increases is accompanied by approximately equal and opposite changes in the methyl and methylene content. The replacement of terminal methyl groups with methylene and the increase in oxide content result in a twofold increase in mechanical strength as k increases. Our study indicates that DEMS provides the best mechanical properties at all k values tested, with hardness/modulus increasing from approximately 1.75 / 10.0 GPa at k=2.7 to approximately 3.45 / 21.3 GPa at k=3.2. Increases in both Si-O and methylene content play roles in the significant improvement in mechanical strength with increasing k. It has been suggested [3, 6, 7] that it is preferable to have all the essential elements of the final film contained within the precursor itself to allow for optimization film structure. DEMS, with a single methyl group per Si and two Si-O groups, is structurally and compositionally the most similar of any precursor to the potential optimum structure seen in this study.

Conclusions

Organosilicate glass films produced by PECVD are leading candidates for next generation integrated circuits. While the various precursors provide films of similar composition and k, their mechanical properties and bonding structure are quite different. Mechanical properties tracked primarily with Si-O content with methylene species also contributing. This suggests that while k may be dominated by the film composition, mechanical properties appear to be dictated by bonding structure and ultimately by the structure of the precursor. Identifying precursors that provide the optimal balance between electrical and mechanical properties will maximize the potential for extension to future ILD generations.

References

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Acknowledgements